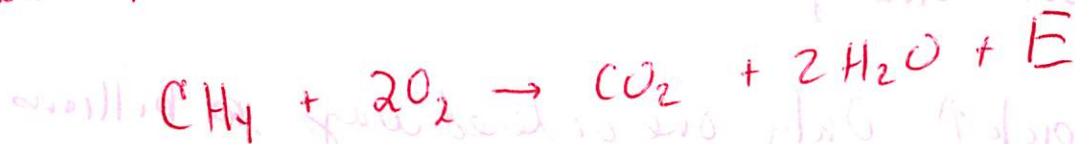


Ch 16 Spontaneity, Free E, Entropy ^①

Last Part of thermochem - (2) pages

1st Part 1st Law of Thermochem - LCE

Did DH calcs before



Could answer Q's

How much E involved in change?

Does E flow in or out of system?

What form does the E finally assume?

LCE gives no indication why it took place.

16.1 Spontaneity \rightarrow spontaneous & occurs w/o continual outside influence.

fast/slow \rightarrow can't tell just if it will take place.

Rates are not governed by Spontaneity

Ex of spontaneous Processes

• Ball down hill, not \uparrow

• Gas uniformly fills container, not collecting

• Heat flows hot to cold

• Wood Burns

• Ice Melts above 0°C

All spontaneous properties are dependent on

Entropy (S) \rightarrow Spont process leads to higher S

(measure of molecular Randomness / disorder)

Classic Bedroom example

Playing 52 pick \uparrow . Only one ordered way ~~in~~ billions of disordered ways.

Entropy values describe the # of arrangements

that are available to a system @ a given state

~~with look~~ \rightarrow Nature spontaneously proceeds to ~~more~~ ^{more} disordered

States that have the highest probability of existing

Gas Container example

Why do ideal gases diffuse?

Simplify

\rightarrow Option 3 is most probable b/c most microstates

See gas example in Fig 16.4

Table 16.1

Table 16.2 show probability of finding molecules dispersed w/ container.

These are all positional Prob

As you would guess $S(s) < S(l) < S(g)$

affects ~~solid~~ solutions b/c mixed substances have higher # of micro states.

16.2 S + 2nd Law of Thermo

In any spontaneous process there is an increase in ΔS of universe

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} \quad (LE say \Delta E_{univ} = 0)$$

$$\frac{\Delta H}{T} = \Delta S_{univ} (+) \text{ spont}$$

$$\Delta S_{univ} (-) \text{ not spont}$$

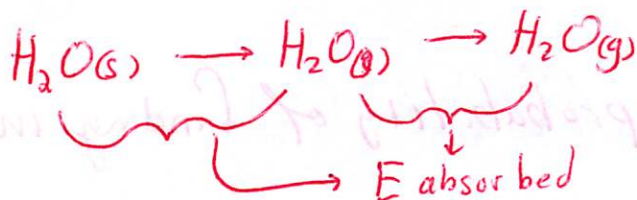
$$\Delta S_{univ} = 0 \rightarrow @ Eq$$

to see if process

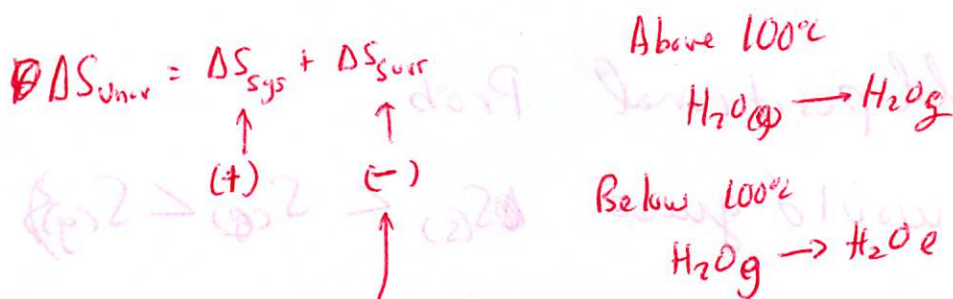
is Spont \rightarrow look @ $S_{sys} + S_{surr}$

16.3 Temp on Spontaneity

↳ Can change spontaneity of processes



But happens spontaneously!



Entropy change Depend on Heat Flow

Exothermic Rxns increase S in surroundings during the Rxns.

↳ Greater impact @ lower T 's

2 main Pts

1. Sign of ΔS depends on heat flow direction

Exothermic vs. Endothermic

2. Mag of ΔS is T dep.

↳ higher @ low T 's

$$\Delta S_{\text{sur}} = \frac{-\Delta H}{T}$$

more (+)
more (-)

higher ΔS
@ lower T 's

See table 16.3

16.4 Free E - Evaluates $\Delta H + \Delta S$ to see how much extra E there is to see if a spontaneous process

For a Rxn @ const T $\Delta G = \Delta H - T\Delta S$
all for system

$-\Delta G$ means spontaneous

$$-\frac{\Delta G}{T} = -\frac{\Delta H}{T} + \Delta S_{sys} \rightarrow -\frac{\Delta G}{T} = \underbrace{\Delta S_{surr} + \Delta S_{sys}}_{\Delta S_{univ}}$$

$-\frac{\Delta G}{T} = \Delta S_{univ}$

So a (-) ΔG ~~means~~ it means spontaneity.
b/c $+\Delta S_{univ}$

$-\Delta G = +\Delta S_{univ}$
2nd law

Do ΔG Probs for physical processes

$\Delta S + Rxns$

Positional Entropy

Make Predictions



Dominated by # of gas Reactants + Products

Book talks ΔG_f° , physical ΔS

Then ΔG for Chemical

Every thing has entropy even elements

Third Law of Thermo \rightarrow Entropy of perfect crystal at 0 K is zero

\hookrightarrow perfect arrangement

once $T \uparrow$ there is some disorder

We aren't going into calc of S° values for things

\odot Too Complicated will just begin see appendix

But can calculations can be done

from S° at 298 K
1 atm

Compare S° values diamond low
graphite high

$$\Delta S^\circ_{\text{Rxn}} = \sum n_p S^\circ_{\text{prod}} - \sum n_r S^\circ_{\text{reactions}}$$

Can Calculate ΔG° , ΔH° , ΔS° @ any condition

$$\Delta G = \Delta H - T\Delta S$$
$$\Delta G = \sum \Delta G_{\text{prod}} - \sum \Delta G_{\text{reac}}$$

\rightarrow using ΔG 's of known rxns



Can't measure ΔG directly. It must be calculated.

Why important?

1. Give idea of likelihood of Rxn to occur
2. Give indication of how far to the Right/Left a Rxn is in Eq.

(Just B/c Reaction Thermodynamically likely is it feasible \rightarrow Kinetics)

16.7 A system @ const $T + P$ will spontaneously proceed in direction that has lowest free E .

The E_g position has the lowest free E value for a particular Rxn System. (Fig 16.7)

Free E depends on $P + [T] \left(+ \frac{H_{\text{mole}}}{KJ_{\text{mole}}} \right) (\Delta S_{\text{for}})$

So it has been shown (Not deriving in book)

$$G = G^0 + RT \ln(P)$$

\uparrow standard

$H_{\text{mole}} @$

P_{atm}

T Kelvin

$R_{\text{univ}} (8.314 \text{ J})$

So for Rxn



$$\Delta G = \sum n G_{\text{prod}} - \sum n G_{\text{react}}$$

$$\Delta G = 2 G_{\text{NH}_3} - G_{\text{N}_2} - 3 G_{\text{H}_2}$$

$$\Delta G = 2 (G_{\text{NH}_3}^0 + RT \ln P_{\text{NH}_3}) - (G_{\text{N}_2}^0 + RT \ln P_{\text{N}_2}) - 3 (G_{\text{H}_2}^0 + RT \ln P_{\text{H}_2})$$

$$= 2 G_{\text{NH}_3}^0 - G_{\text{N}_2}^0 - 3 G_{\text{H}_2}^0 + 2 RT \ln P_{\text{NH}_3} - RT \ln P_{\text{N}_2} - 3 RT \ln P_{\text{H}_2}$$

$$= \Delta G^0 + RT \ln \left(\frac{P_{\text{NH}_3}^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3} \right) \leftarrow Q$$

$$\Delta G = \Delta G^0 + RT \ln Q$$

Reactions

ΔG gives no mention of going to completion.

In fact most Reactions go to Equilibrium

B/c lowest Potential E.



(But @ Eq ΔG is lowest so



However So ΔG tells us if products or Reactants are

favored. Not gone to completion

ΔG° can tell us when Eq will Be

$$\Delta G = \sum (G_{\text{products}}) - \sum (G_{\text{reactants}})$$

$$\Delta G = 3G_{\text{CH}_3\text{OH}} + G_{\text{H}_2\text{O}} - 3G_{\text{H}_2} - G_{\text{CO}} - 3RT \ln Q$$

$$\Delta G = 3G_{\text{CH}_3\text{OH}} + G_{\text{H}_2\text{O}} - 3G_{\text{H}_2} - G_{\text{CO}} - 3RT \ln Q$$

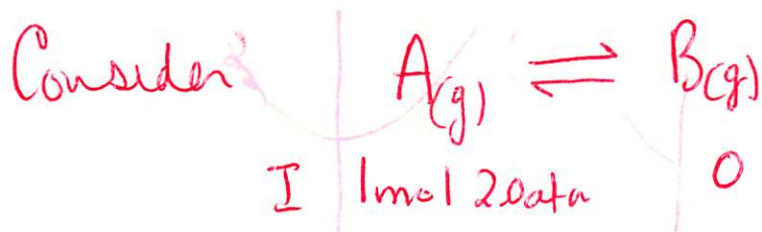
$$\Delta G = \Delta G^\circ + RT \ln Q$$

16.8 ΔG + Equilibrium

Ch 13 \rightarrow Eq as pt @ which $F_{\text{wd}} + P_{\text{ext}} R_{\text{xn}}$ @ same Rate

Ch 16 \rightarrow Eq @ lowest value of Free E.

Both True



As Rxn proceeds $G_A = G_A^0 + RT \ln(P_A)$

$$G_B = G_B^0 + RT \ln(P_B)$$

Total $\rightarrow G = G_A + G_B$

As Eq is reached, The Rxn will proceed until no more Free E Δ

@ (Eq) $\rightarrow P_A^e$ & P_B^e are achieved to make $G_A = G_B$
 \uparrow
 different P's but same G's thus $\Delta G = 0$ @ Eq.

Since $\Delta G = 0$ No driving force to change A to B, B to A so

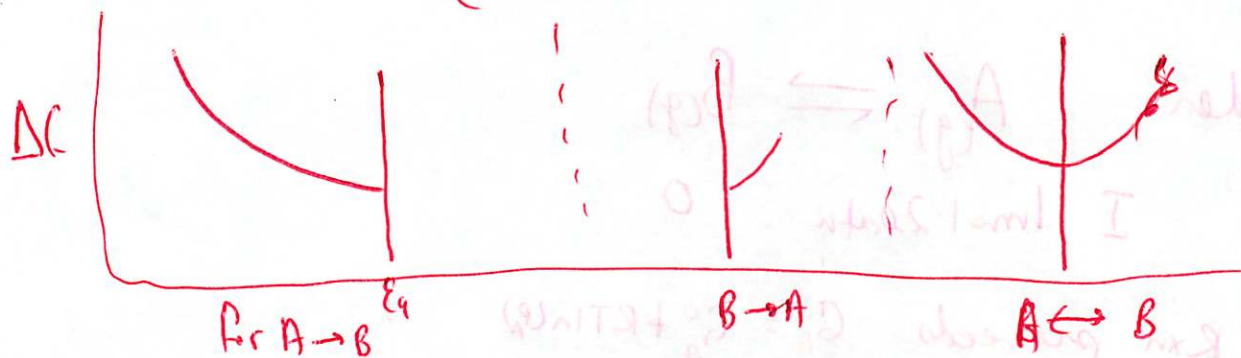
P is constant

Fig 16.9 Assume using mol fraction of A

Say min ΔG is reached when 75% A is reacted

$$@ E_q A (0.25)(2.0 \text{ atm}) = \boxed{0.50 \text{ atm A}}$$

$$B (0.75)(2.0 \text{ atm}) = (1.50 \text{ atm B})$$



Since this @ E_q

$$K = \frac{P_B^x}{P_A^x} = \frac{1.50 \text{ atm}}{0.50 \text{ atm}} = 3.0$$

So for any Reaction the rxn proceeds until min G (E_q) which

corresponds to $G_{rea} = G_{prod}$ $\Delta G = G_{prod} - G_{rea} = 0$

$$\Delta G = \Delta G^\circ + RT \ln Q$$

6

@ Eq $\Delta G = 0$ These

$$\Delta G^\circ = -RT \ln K$$

$$\Delta G^\circ = 0 \quad K = 1$$

B/c $\Delta G_{\text{prod}} > \Delta G_{\text{react}}$ so Rxn must shift

Right to Reach Eq

L

$$\Delta G^\circ > 0 \quad K < 1$$

$$\Delta G^\circ < 0 \quad K > 1$$

B/c $\Delta G_{\text{react}} > \Delta G_{\text{prod}}$ Rxn must shift

Left to Reach Eq.

Systems adjust to lowest

Free E to Reach Eq.

K is dependant on T

$$\Delta G^\circ = -RT \ln(K)$$

$$\Delta H - T\Delta S^\circ = -RT \ln(K)$$

$$\ln(K) = \frac{\Delta H - T\Delta S}{-RT}$$

$$\ln(K) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

$$\ln(K) = -\frac{\Delta H}{R} \left(\frac{1}{T}\right) + \frac{\Delta S}{R}$$

$$y = -m x + B$$

